

AD-A078 537

OKLAHOMA UNIV NORMAN DEPT OF CHEMISTRY  
OXY- AND THIO- PHOSPHORUS ACID DERIVATIVES OF TIN. III. THE X-R--ETC(U)  
NOV 79 M B HOSSAIN , J L LEFFERTS  
TR-14

F/G 7/3

N00014-77-C-0432

NL

UNCLASSIFIED

|OF|

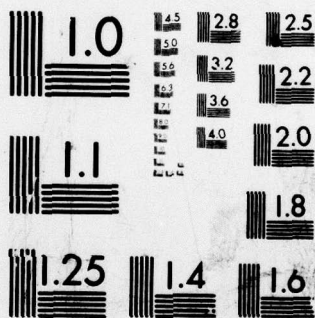
AD  
A078537



END  
DATE  
FILMED

1-80

DDC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

ADA 078537

(12) LEVEL II

9079679

OFFICE OF NAVAL RESEARCH

Contract N00014-77-C-0432

Task No. NR 053-636

TECHNICAL REPORT NO. 14

Oxy- and Thio- Phosphorus Acid Derivatives of Tin. III.  
The X-ray Crystal and Molecular Structure of Bis-( $\sigma, \sigma'$ -  
-Diphenyldithiophosphato)tin(II),  $\text{Sn}(\text{S}_2\text{P}(\text{OC}_6\text{H}_5)_2)_2$ , a  
Bicyclic Dimer Held Together by  $\text{h}^6\text{-C}_6\text{H}_5$  to Tin(II) Interactions

by

M.B. Hossain, J.L. Lefferts, K.C. Molloy, D. van der Helm  
and J.J. Zuckerman

in

Angewante Chemie

11 12 Nov 79

12 11

University of Oklahoma  
Department of Chemistry  
Norman, Oklahoma 73019

DDC  
RECEIVED  
DEC 18 1979  
B

Reproduction in whole or in part is permitted for  
any purpose of the United States Government

\*This document has been approved for public release  
and sale; its distribution is unlimited

DDC FILE COPY

79 12 11 140  
403980

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 14	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Oxy- and Thio- Phosphorus Acid Derivatives of Tin. III. The X-ray Crystal and Molecular Structure of Bis-[ $\text{O}, \text{O}'$ -Diphenyldithiophosphato]tin(II), $\text{Sn}$ [ $\text{S}_2\text{P}(\text{OC}_6\text{H}_5)_2$ ] $_2$ a Bicyclic Dimer Held Together by		5. TYPE OF REPORT & PERIOD COVERED
7. AUTHOR(s) $\text{h}^6\text{-C}_6\text{H}_5$ to Tin(II) Interactions M.B. Hossain, J.L. Lefferts, K.C. Molloy, D. van der Helm and J. J. Zuckerman		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Oklahoma Department of Chemistry Norman, Oklahoma 73019		8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0432
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of Navy Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-636
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE 12 November, 1979
		13. NUMBER OF PAGES 8
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  Approved for Public Release, Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  Prepared for publication in Angewante Chemie		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Fin, Phosphoric Acids. Dithiophosphoric Acids, X-ray Diffraction, Crystal Structure, Molecular Structure, Dithiophosphate Ester Ligands, Divalent tin, Centrosymmetric Dimer, Anisobidentate Chelation, $\text{h}^6$ -Phenyl Interaction with (Tin(II) Lone Pair, $\pi$ -Interaction, Cyclic $\text{Sn}_2\text{S}_2$ System, Bridging Sulfur		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Bio-[ $\text{O}, \text{O}'$ -diphenyldithiophosphato]tin(II), $\text{C}_{24}\text{H}_{20}\text{O}_4\text{P}_2\text{S}_4\text{Sn}$ crystallizes in the triclinic space group $\text{P}\bar{1}$ with $a=10.499(5)$ , $b=13.948(7)$ , $c=9.291(4)\text{\AA}$ ; $\alpha=99.18(6)^\circ$ , $\beta=95.71(5)^\circ$ , $\gamma=91.80(5)^\circ$ . The structure was studied by Monochromated Mo-K $\alpha$ radiation and refined to a final R value of 2.9% for 5517 reflections. The centrosymmetric, dimer contains one ligand bridging two tin atoms intermolecularly while simultaneously chelating one tin atom in an extremely anisobidentate manner. A planar $\text{Sn}_2\text{S}_2$ four-membered ring is circumscribed by an $(\text{SnSPS})_2$		

A

P1

eight-membered ring. The dimer is in addition held together by a long  $\pi$ -interaction of 3.46 Å along and S-Sn vector to be the center of one of the aromatic rings of an ester group of the bridging ligand of the second monomeric unit. This ring is oriented in a spacially significant position perpendicular to the assumed vector of the tin lone pair producing a distorted octahedral (4-6) geometry at the metal center and the sole example of a  $h^6-C_6H_5$  main group  $\pi$ -bond known, especially one contributing to the formation of a dimer.

ACCESSION for	
NTIS	White Section <input checked="" type="checkbox"/>
DDC	Buff Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION _____	
BY _____	
DISTRIBUTION/AVAILABILITY CODES	
Dist. Avail. Only of SPECIAL	
A	



Oxy- and Thio- Phosphorus Acid Derivatives of Tin. III.

The X-ray Crystal and Molecular Structure of Bis-[0,0'-

Diphenyldithiophosphato]tin(II),  $\text{Sn}[\text{S}_2\text{P}(\text{OC}_6\text{H}_5)_2]_2$ , a

Bicyclic Dimer Held Together by  $\text{h}^6\text{-C}_6\text{H}_5$  to Tin(II) Interactions [\*\*]

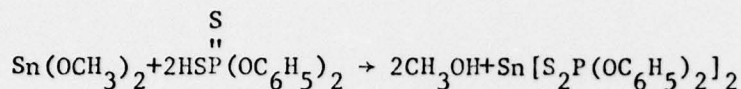
By H.B. Hossain, J.L. Lefferts, K.C. Molloy, D. van der Helm and

J.J. Zuckerman [\*]

[\*] Drs. M.B. Hossain, J.L. Lefferts, K.C. Molloy, Prof. Dr. D. van der Helm, J. J. Zuckerman, University of Oklahoma, Department of Chemistry, Norman, OK 73019 (USA).

[\*\*] Our work is supported by the U.S. Office of Naval Research (J.J.Z.) and the National Cancer Institute, U.S. D.H.E.W. through Grant No. CA-17562 (D.v.d.H).

The tin(II) dithiophosphate ester  $\text{Sn}[\text{S}_2\text{P}(\text{OC}_6\text{H}_5)_2]_2$  (m.p. 125.5–126.5°C) has been synthesized by the reaction of dimethoxytin(II) with two equivalents of 0,0'-diphenyldithiophosphoric acid in benzene:



and characterized by  $^{119\text{m}}\text{Sn}$  Mössbauer [I.S.=3.78±0.02; Q.S.=1.06±0.04mm/s] and mass [highest observed m/e=682(2.9%)M<sup>+</sup>] spectroscopies as well as microanalyses [Found: C, 42.50; H, 3.10%. Calc'd. for  $\text{C}_{24}\text{H}_{20}\text{O}_4\text{P}_2\text{S}_4\text{Sn}$ : C, 42.31; H, 2.96%]. A triclinic single crystal of space group  $\text{P}\bar{1}$  [a=10.499(5), b=13.948(7), c=9.291(4)Å; α=99.18(6)°, β=95.71(5)°, γ=91.80(5)°] was studied by Mo-K<sub>α</sub> X-radiation and refined to a final R value of 2.9% for 5517 reflections.

The centrosymmetric dimer shown in Fig. 1 contains one ligand bridging two tin atoms intermolecularly while simultaneously chelating one tin atom in an extremely anisobidentate fashion, via the three-coordinated (S4). A second ligand is involved in normal anisobidentate chelation as is found in the tin(II) dithiocarbamate,  $\text{Sn}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$ <sup>[1]</sup> and dithiocarbonate,  $\text{Sn}[\text{S}_2\text{COCH}_3]_2$ <sup>[2]</sup>. A planar  $\text{Sn}_2\text{S}_2$  four membered ring such as is found in  $\text{Sn}_2\text{S}_3$ <sup>[3]</sup> and  $(\text{CH}_3\text{Sn})_4\text{S}_6$ <sup>[4]</sup> is circumscribed by an  $[\text{SnSPS}]_2$  eight-membered ring in an arrangement reminiscent of the eight-membered centrosymmetric rings formed by the tin(IV) atoms and dichlorophosphate groups in the dimeric  $[\text{Cl}_3\text{SnPO}_2\text{Cl}_2 \cdot \text{POCl}_3]_2$ <sup>[5]</sup>. Our structure contrasts with those adopted by lead(II) diethyldithiophosphate in which the metal atoms are chelated in monomers<sup>[6]</sup>, and its diisopropyl analogue in which the metal atom is coordinated by six sulfur atoms, two of which bonded intermolecularly to give a polymeric lattice<sup>[7]</sup>.

Unlike these structures, the dimeric title compound is held together by two coordinate bonds at 3.0248(7) emanating from S(4) or S(4') atoms plus a long  $\pi$ -interaction at 3.46 $\overset{\circ}{\text{A}}$  along the S(3)-Sn vector to the center of one of the aromatic rings of an ester group of the bridging ligand of the second monomeric unit. This ring is oriented in a spatially significant position perpendicular to the assumed vector of the tin lone pair producing a distorted octahedral ( $\psi$ -6) geometry at the metal center.  $\pi$ -Interactions with tin(II) lone pairs are found in  $\underline{\text{h}}^6\text{-C}_6\text{H}_6\text{Sn(AlCl}_4)_2\cdot\text{C}_6\text{H}_6$  [8-10] and  $\underline{\text{h}}^6\text{-C}_6\text{H}_6\text{SnCl(AlCl}_4)$  [11-12] where the distances to the center of the rings lie in the range 2.74 to 2.90 $\overset{\circ}{\text{A}}$ , long with respect to transition metal-arene distances. Our dimer is unique however, for two reasons. Firstly, to our knowledge [13] we have here the only example of an  $\underline{\text{h}}^6\text{-C}_6\text{H}_5$  main group  $\pi$ -bond; and secondly, the only known example of such an interaction contributing to the formation of a dimer from the constituent monomers.

The existence of the  $\text{Sn}_2\text{S}_2$  ring is confirmed on close inspection of the phosphorus-sulfur distances. The more tightly bound to a metal the dithiophosphate sulfur is, then the longer its bond to phosphorus. [14] For example, in the purely chelating ligands in our structure atom S(1) makes a short tin bond [S(1)-Sn(1)=2.6230(6)] and a long bond to phosphorus [S(1)-P(1)=2.0016(8) $\overset{\circ}{\text{A}}$ ]. Atom S(2) does the opposite [S(2)-Sn(1)=2.8300(6); S(2)-P(1)=1.9670(8) $\overset{\circ}{\text{A}}$ ]. Thus we conclude that atom S(2) is double-bonded to P(1). However, comparison of the two ligands bonded to each tin atom reveals that although the bridging sulfur-tin bond is significantly longer [S(4)-Sn(1)=3.0248(7)] than the corresponding chelating bond [S(2)-Sn(1)=2.8300(6)], the presumably P=S distances are quite similar [P(2)=S(4)=1.9636(8); P(1)=S(2)=1.9670(8) $\overset{\circ}{\text{A}}$ ]. This unexpectedly long P(2)=S(4) distance must arise because of the electron withdrawal along the S(4)-Sn(1) vector at 3.3914(6) $\overset{\circ}{\text{A}}$ , thus confirming the interaction between these two atoms. In  $[\text{CuS}_2\text{P(OC}_3\text{H}_7\text{-iso)}_3]_4$ , on the other hand, the three-



coordinated sulfur atoms that bridge two metal centers form equal or stronger sulfur-metal bonds than the sulfurs bonded to only one metal atom. In that case electron withdrawal from the bridging sulfur-phosphorus  $P=S$  bond so lengthens this distance that it actually becomes longer than the adjacent  $P-S$  single bond. [15]

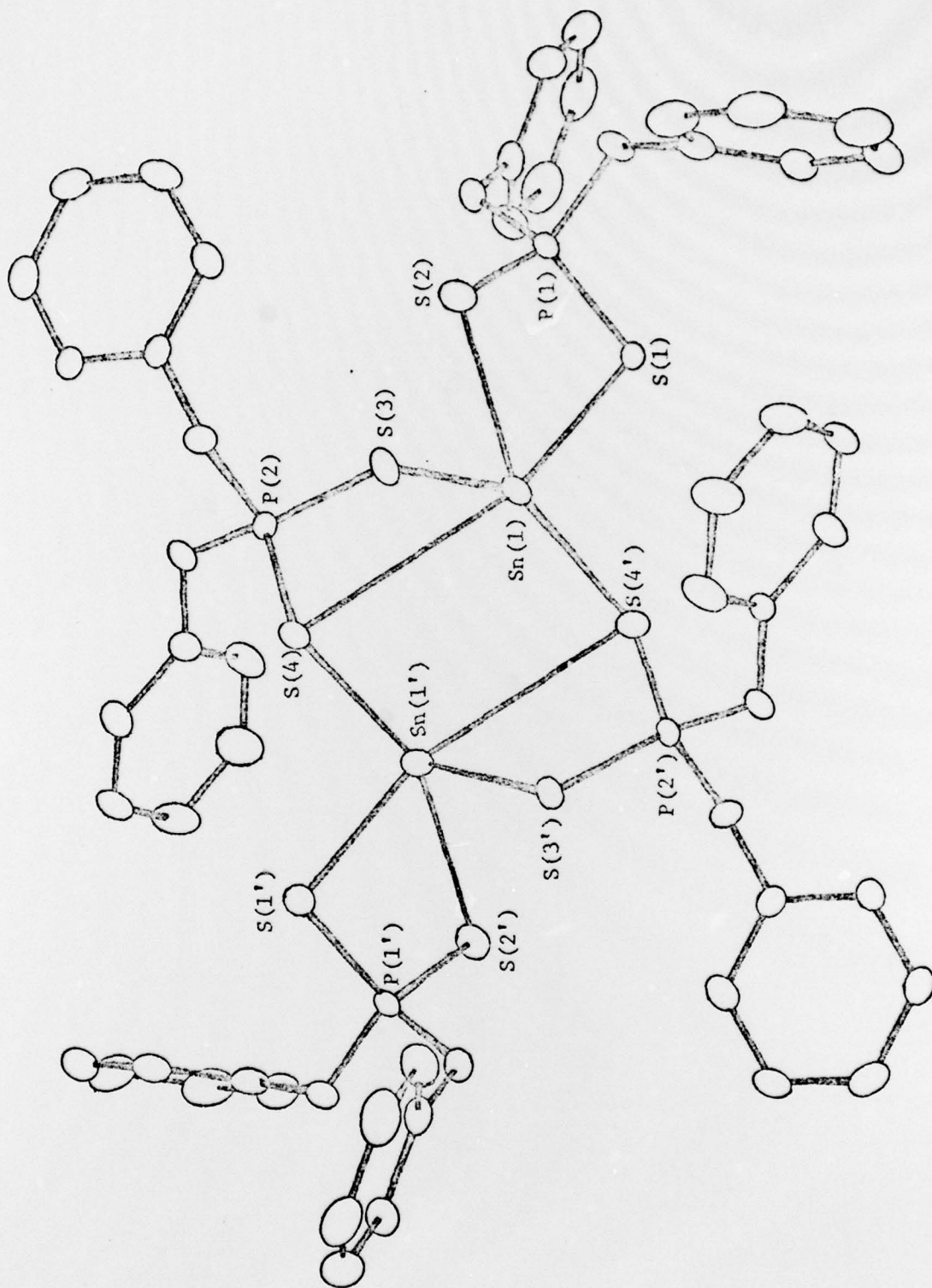
- [1] J. Potenze, D. Mastropaolo, *Acta Crystallogr.*, B29, 1830 (1973).
- [2] P.R.R. Ewings, P.G. Harrison, T.J. King, *J. Chem. Soc., Dalton Trans.*, 1399 (1976).
- [3] D. Movtz, R. Kunzmann, *Acta Crystallogr.*, 15, 913(1962); 23, 471(1967).
- [4] C. Dorfelt, A. Janeck, D. Kobelt, E.F. Paulus, H. Scherer, *J. Organometal. Chem.* 14, P22(1968).
- [5] D. Moras, A. Mitschler, R. Weiss, *Acta Crystallogr.*, B25, 1720(1969); B25, 1726(1969).
- [6] T. Ito, *Acta Crystallogr.*, B28, 1034(1972).
- [7] S.L. Lawton, G.T. Kokotailo, *Nature*, 221, 550(1969).
- [8] Th. Auel, E.L. Amma, *J. Am. Chem. Soc.*, 90, 5941(1978).
- [9] H. Lüth, E.L. Amma, *J. Am. Chem. Soc.*, 91, 7515(1969).
- [10] P.F. Rodesiler, Th. Auel, E.L. Amma, *J. Am. Chem. Soc.*, 97, 7405 (1975).
- [11] M.S. Weininger, P.F. Rodesiler, A.G. Gash, E.L. Amma, *J. Am. Chem. Soc.*, 94, 2135(1972).
- [12] M.S. Weininger, P.F. Rodesiler, E.L. Amma, *Inorg. Chem.*, 18, 751(1978).
- [13] J.A. Zubieta, J.J. Zuckerman, *Prog. Inorg. Chem.*, 24, 251(1978).
- [14] J.R. Wasson, G.M. Woltermann, H.J. Stoklosa, *Fortschr. Chem. Forsch.*, 35, 65(1973).
- [15] S.L. Lawton, W.J. Rohrbaugh, G.T. Kokotailo, *Inorg. Chem.*, 11, 612(1972).

### Figure Captions

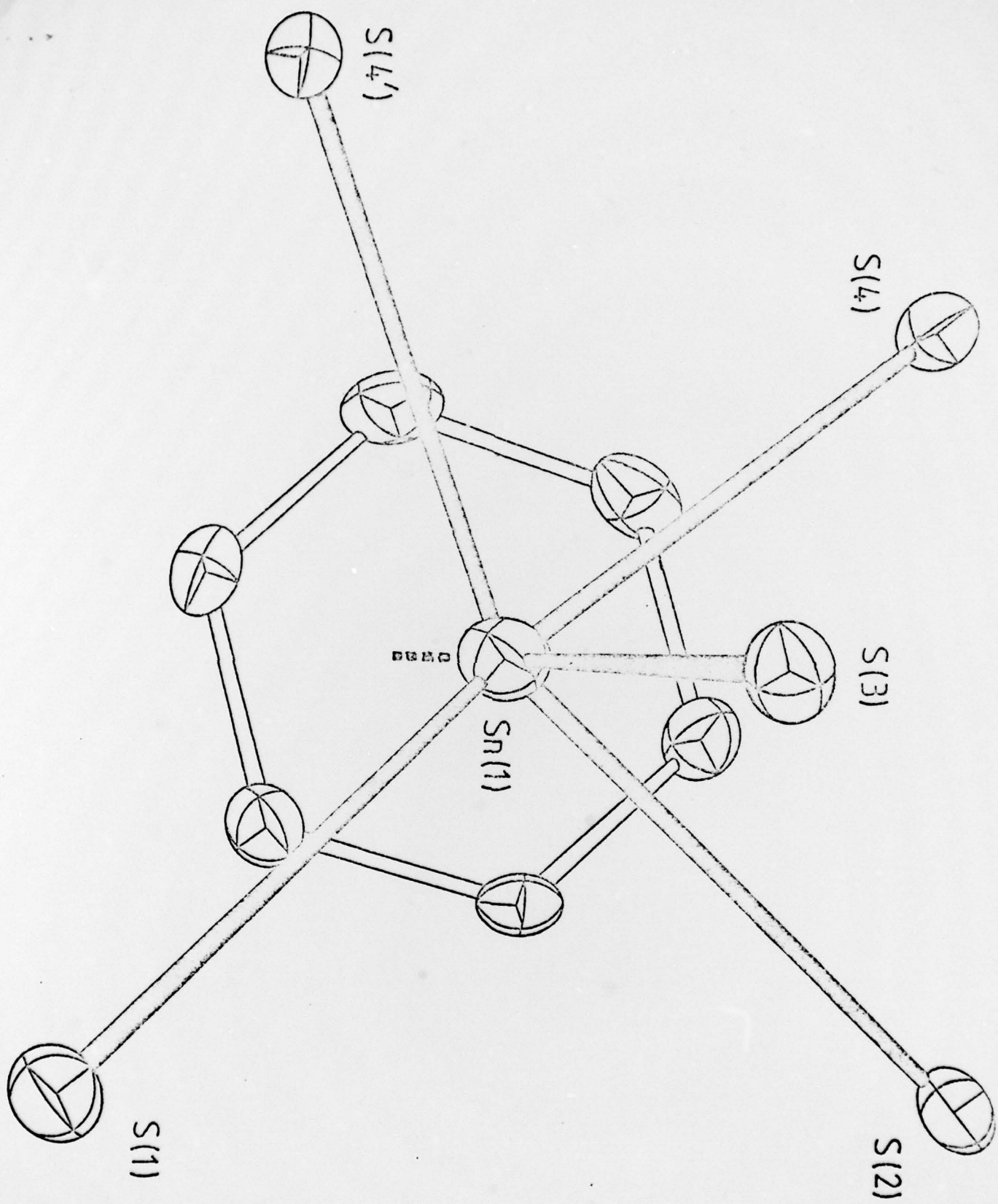
Fig. 1. The dimeric molecular structure of bis-[0,0'diphenyldithiophosphato]tin(II),  $\text{Sn}^{\text{II}}[\text{S}_2\text{P}(\text{OC}_6\text{H}_5)_2]_2$ , held together by bifurcated, three-coordinated, sulfur atom bonds and  $\text{h}^6\text{-C}_6\text{H}_5$  interactions with the tin(II) lone electron pairs.

Fig. 2. The  $\text{h}^6\text{-C}_6\text{H}_5\text{-tin(II)}$  vector. The distance to the center of the ring is 3.46Å.









80